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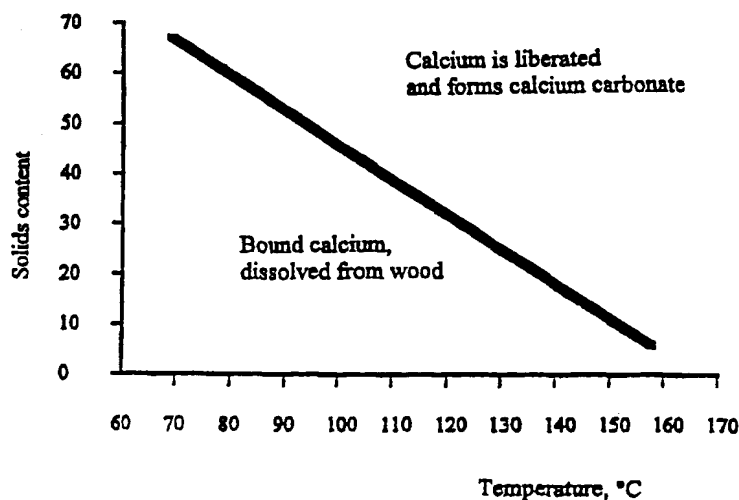
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: METHOD FOR THE TREATMENT OF SPENT LIQUOR FROM KRAFT PULP PRODUCTION

## (57) Abstract

When pulp is manufactured by so-called modified cooking methods, spent liquor is formed containing large amounts of calcium bound to the dissolved material. During evaporation calcium is liberated and precipitates on the heat transfer surfaces of the evaporating plant. By means of the method according to the invention the precipitation of calcium is either moved to a stage in the evaporating process where it co-precipitates with sodium salts, whereby the precipitate is easily dissolved, or the calcium is deactivated prior to the evaporating plant by allowing it to precipitate at a stage where no scaling can be formed on heat transfer surfaces.

**Liberation of calcium from dissolved wood material as a function of temperature and solids content**

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## METHOD FOR THE TREATMENT OF SPENT LIQUOR FROM KRAFT PULP PRODUCTION

### Field of the invention

- 5 The invention relates to a method for the treatment of spent liquor generated in kraft pulp production, in which method spent liquor is treated following kraft pulp production at the black liquor evaporation plant or prior to evaporation. Particularly, by means of said method the formation of scale on heat exchanger surfaces is avoided.

### 10 Background of the invention

In the kraft process, cellulose-containing material like wood is treated at elevated temperature with alkaline cooking liquor containing sodium hydroxide and sodium hydrogen sulfide. Fresh, inorganic cooking liquor is called white liquor, and spent liquor containing material dissolved from the starting material, e.g. wood, is called black liquor.

- 15 Through evaporation, incineration and causticization, white liquor is regenerated from the chemicals contained in the black liquor.

Traditionally, both in the case of batch cooking processes and continuously operated processes, the black liquor led to the evaporation plant originates directly from the main  
20 cooking stage, where it has been generated during said stage.

In search for improved pulp properties, cooking methods have been developed wherein the black liquor feed of the evaporation plant is recycled black liquor originating from the early stages of the cooking sequence. Such processes have been disclosed in, e.g. patent publications FI 93866 and FI 92224. In yet other types of processes, the black liquor led to  
25 the evaporation plant has formed during the whole cooking process, but the cooking temperature has been significantly lowered relative to the temperatures of a traditional cook. In such a cook, called an extended cook, it may occur that the temperature of the spent liquor does not, at any stage of the process, exceed 160 °C. These cooking processes are hereinafter referred to as modified cooking processes.

- 30 In the cooking process, material containing bound calcium usually dissolves from the starting material into the cooking liquor. The properties of the black liquor entering the evaporation plant in a modified cooking process differ from those of a traditional cook, and may complicate the evaporation of black liquor. This is particularly severe if it is desired to

treat the cellulose-containing material entering the kraft process, preferably as wood chips, with a solution containing large amounts of sodium carbonate and only minor amounts of sodium hydroxide and sodium hydrogen sulfide, if any. Most preferably, such a solution is a mixture of the molten chemicals leaving the recovery boiler and weak white liquor, referred to as green liquor.

The black liquor described above, exiting a modified cooking process and bound for the evaporation plant, contains large amounts of calcium bound to the dissolved material. In case the raw material is wood, the dissolved material consists of lignin and other components of wood soluble in the cooking liquor. In traditional cooking methods, the dissolved material degrades due to the alkalinity and raising temperature of the cooking liquor, whereby the bound calcium is liberated, reacting with, e.g. the materials extracted from the raw material thereby forming calcium soaps, and with the carbonate in the cooking liquor forming calcium carbonate.

During a modified cook, there may be only minor degradation of dissolved material, and thus the concentration of calcium in a bound state may be high.

In the kraft process, the solid soaps formed from the extracted material are separated from the black liquor prior to evaporation, and as evaporation proceeds, in order to minimize the disadvantages caused. The bulk of the calcium carbonate formed has already crystallized in the digester, and the solubility of dissolved calcium carbonate increases with temperature. Typically, during the evaporation process, the solids content of the black liquor rises as temperature increases, and there is no significant crystallization of the calcium carbonate entering the evaporation plant in the black liquor as evaporation proceeds; thus, normally no problems are caused by precipitation on the evaporator heat transfer surfaces that would limit the plant's capacity of evaporating water from the black liquor.

In current evaporating plants used for evaporating black liquor from modified cooking processes, the dissolved material is degraded further as evaporation proceeds and the solids content and temperature both rise. The calcium bound to the dissolved material is thereby set free. The liberated calcium reacts with the carbonate in the black liquor, forming calcium carbonate. A significant amount of crystallization occurs on the plant's heat transfer

surfaces, whereby the plant's water evaporation capacity is severely limited. Crystallization may be so extensive, that the heat transfer surfaces must be repeatedly cleaned, which requires special procedures, calling for a plant shutdown or limitation of normal production.

5

In the article "Evaporator scaling" by T.M. Grace, *Southern Pulp and Paper Manufacturer*, August 1977, 16-23, a method is disclosed wherein spent liquor is thermally deactivated with respect to calcium by directing it, between evaporator stages, into a tank equipped with a heating circuit, and adding free calcium carbonate to the tank as required for  
10 crystallization to take place. The deactivation stage is provided immediately before the evaporation stage where scaling is most severe. When the liquor is returned to the evaporating plant after the deactivation stage, its heat content is so large that it is directed to the hottest evaporation unit, and then in concurrent flow down the evaporating plant.

According to the cited article, a separate deactivation unit must be provided adjacent to the  
15 evaporation plant, raising investment and running costs. The system further comprises a unit for the addition of solid calcium carbonate to provide the seeding material as required. As the spent liquor is heated by steam in a heat exchanger, it is likely that the scaling problem is carried over from the evaporation plant to said heat exchanger.

## 20 Disclosure of the invention

### *General description*

According to the present invention, black liquor from a modified kraft cooking process, is treated according to claim 1 without diverting the liquor outside the evaporating plant, whereby the calcium bound to the wood components dissolved in the black liquor is  
25 liberated in a controlled manner, not negatively affecting the evaporation process.

As the liberation of calcium bound to the material dissolved in the black liquor is dependent on the solids content and alkalinity of the black liquor, and on temperature, according to the invention it is preferable to direct the stream of black liquor in the evaporation plant in a  
30 way where the liberation of calcium and the formation of calcium carbonate occurs at a stage of the evaporation process where it does not impede the operation of the evaporation plant. Thus, during evaporation the liquor stream flows from one evaporation unit to the

next in an expedient order. If this is not possible, the black liquor is treated in separate processing equipment prior to the evaporation plant in order to liberate calcium and form calcium carbonate.

5 *Detailed description*

The invention is disclose more closely below, with reference to the enclosed drawings, wherein

Figure 1 represents a solubility chart showing the dependency of the liberation of bound calcium on the solids content and alkalinity and the temperature of a black liquor;

10 Figure 2 shows the sequence of black liquor flow in a six-stage evaporation plant according to the prior art;

Figure 3 represents a solubility chart showing how the critical temperature of calcium liberation is reached in an evaporation plant according to Figure 2;

Figure 4 shows the flow sequence in an evaporation plant according to the invention;

15 Figure 5 shows, by means of a solubility chart, how calcium is liberated when a flow sequence according to Figure 4 is used;

Figure 6 represents an arrangement to deactivate calcium before the black liquor is led to the evaporation plant; and

20 Figure 7 shows, by means of a solubility chart, how calcium is liberated when deactivation at the cooking unit, according to Figure 6, is used.

The liberation of calcium bound to the wood material dissolved in the black liquor depends on the solids content and alkalinity of the black liquor and on temperature, largely as shown in Figure 1. The solubility threshold is not necessarily represented by a straight line, especially not in all liquor compositions; Figure 1 is schematic and indicates the general  
25 tendency, as is the case with corresponding Figures 3, 5 and 7. According to the prior art, black liquor is evaporated in a manner well known to a person skilled in the art, in a multiple-stage, typically a six-stage evaporation plant, wherein the black liquor arriving from the cooking plant is fed to the coldest unit ((6), Figure 2). The black liquor flows  
30 towards the hottest unit ((1), Figure 2), its solids content and alkalinity rising along the way. The numbers in Figure 3 correspond to the evaporating stages. It is apparent from Figure 3, how the critical solids content and temperature for calcium liberation are reached in stage 2

of the evaporator. Calcium precipitates and forms scaling on the heat transfer surfaces of stage 2.

According to one embodiment of the present invention, the black liquor is directed from stage 4 to stage 2, and on to stage 3, from where it is directed to stage 1. Such a flow sequence is shown in Figure 4. In stage 2, the solids content of the liquor is preferably from about 30 to about 35 %, and its temperature from about 110°C to about 120 °C; in stage 3, the solids content of the liquor is preferably from about 35 to about 45 %, and its temperature from about 90°C to about 120 °C. Figure 5 shows how calcium is not yet liberated in stages 2 and 3, only in stage 1. In stage 1, the solids content of the black liquor is so high that the sodium sulfate and sodium carbonate therein starts to form a solid phase generally referred to as double salt. Double salt crystallizes in a much larger amount than calcium carbonate, which thus is prevented from forming a precipitate of its own on the heat transfer surfaces; instead it is included in the extensive crystallization of double salt.

The double salt, on the other hand, is easily dissolved by conveying into the unit, for example, black liquor having a solids content below the solubility limit of the double salt. Though the calcium carbonate does not dissolve into such black liquor, which is typically saturated with calcium carbonate, the calcium carbonate is removed from the evaporator heat transfer surfaces as the surrounding double salt dissolves.

The stage sequence may vary from that disclosed above, there may for example be several evaporation stages following the crossing of the calcium carbonate solubility threshold.

An advantage of the embodiment disclosed above is that there are very moderate costs associated therewith when an existing evaporation plant is updated. A new evaporating plant may be constructed at no extra cost relative to an arrangement according to the prior art.

In case the black liquor temperatures and solids contents of stages 2 and 3 cannot be kept below the critical values using the arrangement described above, according to one embodiment of the invention the black liquor temperature is raised above the critical value for a sufficiently long period in order for the calcium to be liberated and form calcium

carbonate before the black liquor is led to the evaporation plant. This treatment is referred to as calcium deactivation.

Figure 6 shows an arrangement of tanks in a batch displacement kraft cooking plant as disclosed in, for example Finnish Patent 92224. Warm black liquor from black liquor tank (a) is led to heat exchanger (b), where its temperature is raised close to the critical temperature for calcium liberation, using in the heat exchanger hot black liquor from pressurized holding tank (c). After heat exchanger (b), the state of the black liquor is changed in order to cross the critical limit for calcium liberation, by raising the temperature with straight steam heating, and/or by raising the solids content by addition of black liquor higher in solids (d), and/or regulating alkalinity by adding pH-lowering solution from tank (e); said solution may be for example water from a tall oil digestion plant. The black liquor is kept in pressurized holding tank (c) until calcium carbonate has been formed. From the holding tank, the black liquor is directed to the evaporation plant via heat exchanger (b).

Figure 7 shows a solubility chart for an arrangement according to Figure 6. The black liquor leaving tank (a) is in a state corresponding to point (1). After passing heat exchanger (b), the liquor has moved into a state corresponding to point (2); subsequently the liquor is taken across the solubility limit to point (3) (by raising the temperature) or (4) (by raising both solids content and temperature).



Claims

1. A method for the treatment of spent liquor from the manufacturing of kraft pulp, wherein the calcium bound to material dissolved in said liquor, not having reached a sufficiently high  
5 temperature for being liberated during the cooking process, is liberated and forms calcium carbonate, **characterized** by that the spent liquor is brought into a state with respect to its temperature, solids content and alkalinity, such that calcium is liberated from the dissolved material and precipitates essentially as carbonate in a process stage where it does not form scaling of low solubility on the heat transfer surfaces of the apparatus; and that the spent  
10 liquor during the evaporation process is conveyed solely from one evaporating unit to the next.
2. A method according to claim 1, **characterized** by that during concentration of spent liquor in a multistage evaporation plant said liquor is first conveyed from one evaporating  
15 unit to a hotter evaporation unit to be concentrated near the limit for calcium liberation, and is subsequently conveyed to a colder evaporating unit to be further concentrated near the limit for calcium liberation.
3. A method according to claim 2, **characterized** by the spent liquor additionally is  
20 conveyed to at least one evaporating unit where the liquor temperature and solids content are high enough for calcium to be liberated and form calcium carbonate, whereby simultaneously sodium sulfate and sodium carbonate are formed in said evaporating unit.
4. A method according to claim 1, **characterized** by that the spent liquor before being  
25 brought to the evaporating plant is brought, for a sufficient time, into a state where calcium is liberated and forms calcium carbonate.
5. A method according to claim 4, **characterized** by said state is reached by raising the temperature of the spent liquor.

6. A method according to claim 4 or 5, **characterized** by said state being reached by addition to the spent liquor of black liquor having a higher solids content than said spent liquor.

5 7. A method according to any claim 4-6, **characterized** by said state being reached by lowering the alkalinity of the spent liquor.

8. A method according to any claim 4-6, **characterized** by said state being reached by addition to the spent liquor of black liquor having a higher solids content than said spent  
10 liquor.

9. A method according to any claim 4-6, **characterized** by said state being reached by lowering the alkalinity of the spent liquor.

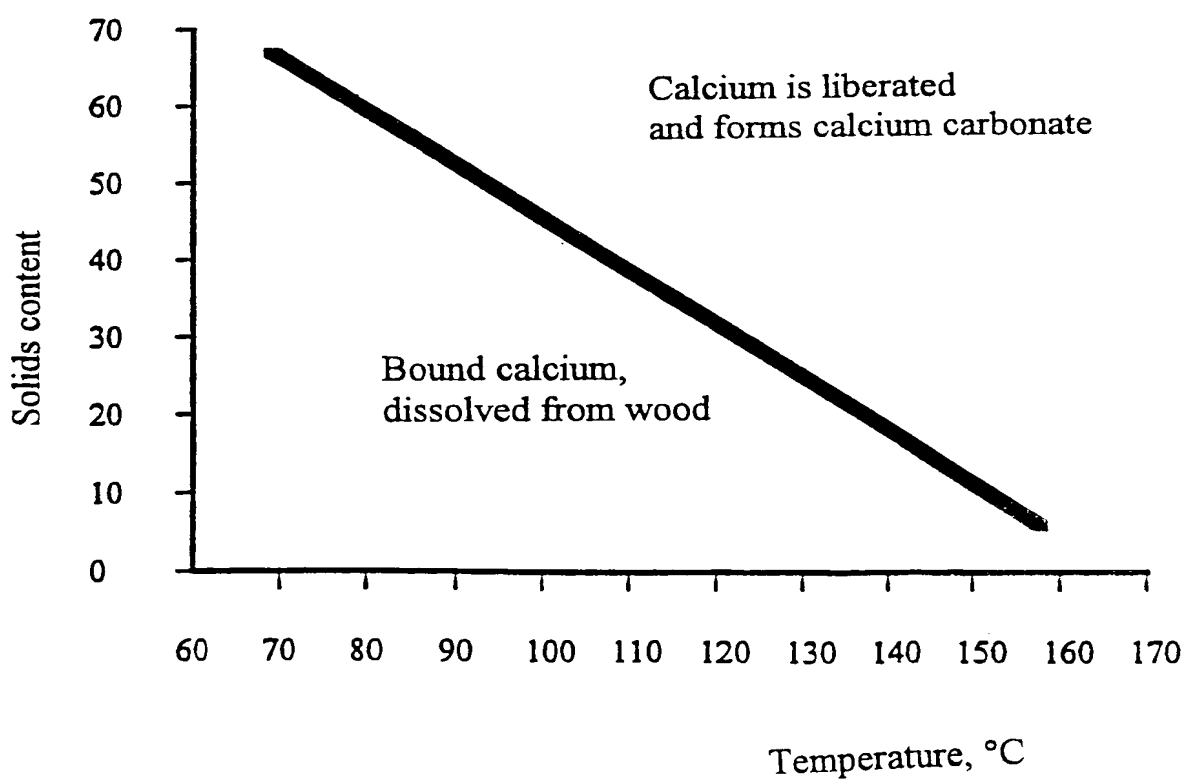
15 10. A method according to any claim 1-9, **characterized** by the spent liquor essentially not having exceeded 160 °C during the cooking process.

11. A method according to any claim 1-10, **characterized** by the raw material of said kraft pulp manufacturing cooking process having been treated with green liquor at the beginning  
20 of the cooking sequence.

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## Fig. 1

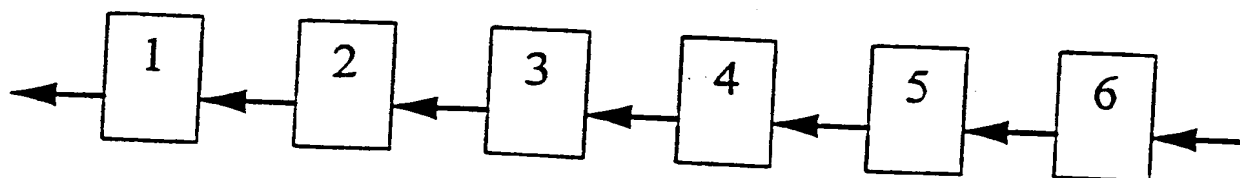
Liberation of calcium from dissolved  
wood material as a function of  
temperature and solids content



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# Fig. 2

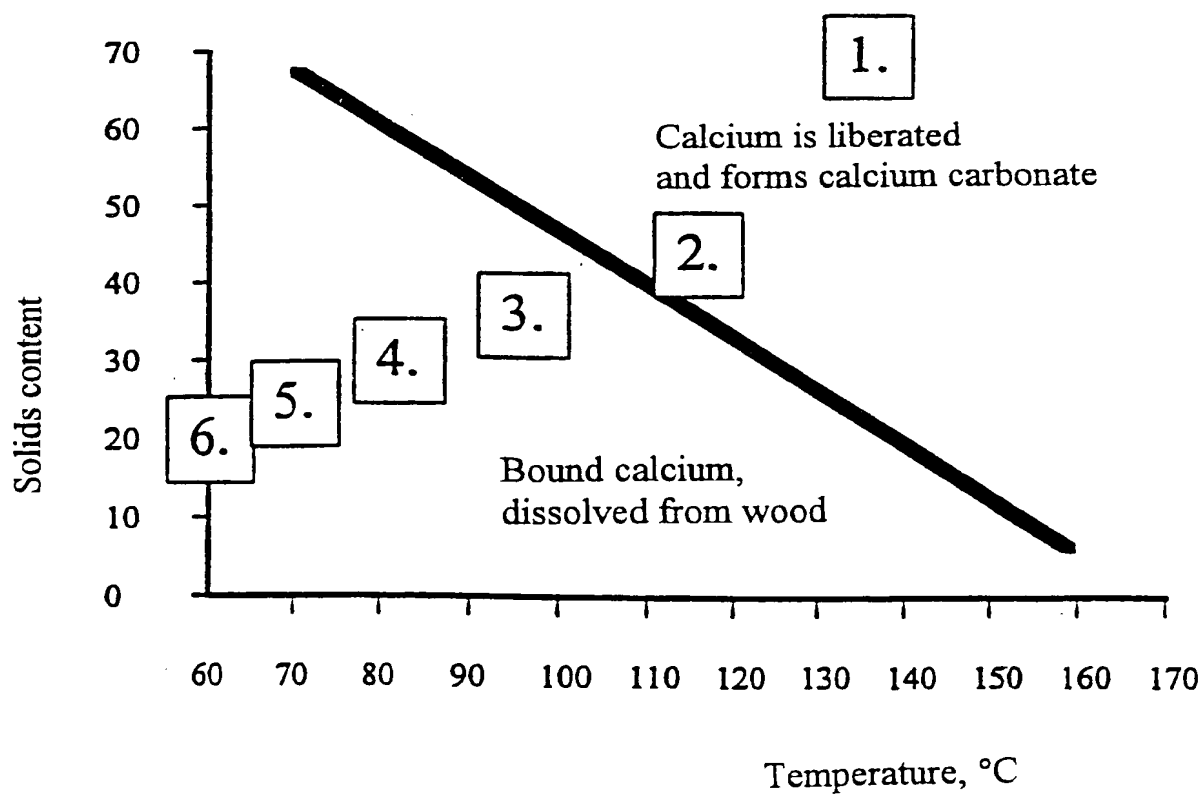
Typical black liquor flow sequence  
in a 6-stage evaporating plant



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## Fig. 3

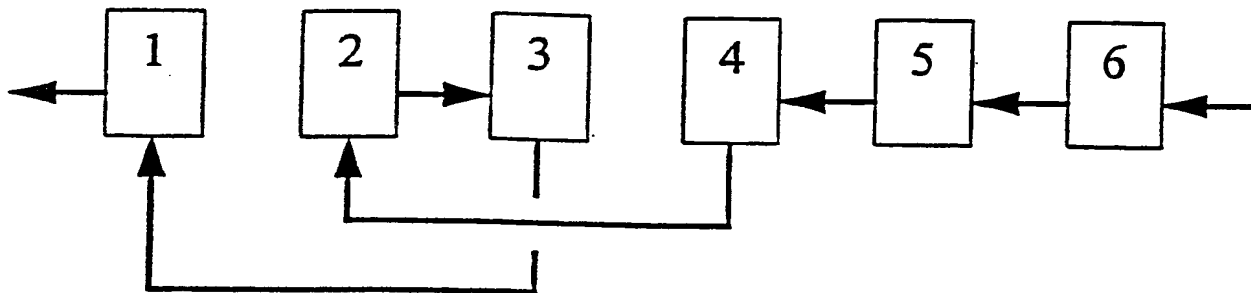
Typical solids/temperature change  
and critical limit in a 6-stage  
evaporation plant



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Fig. 4

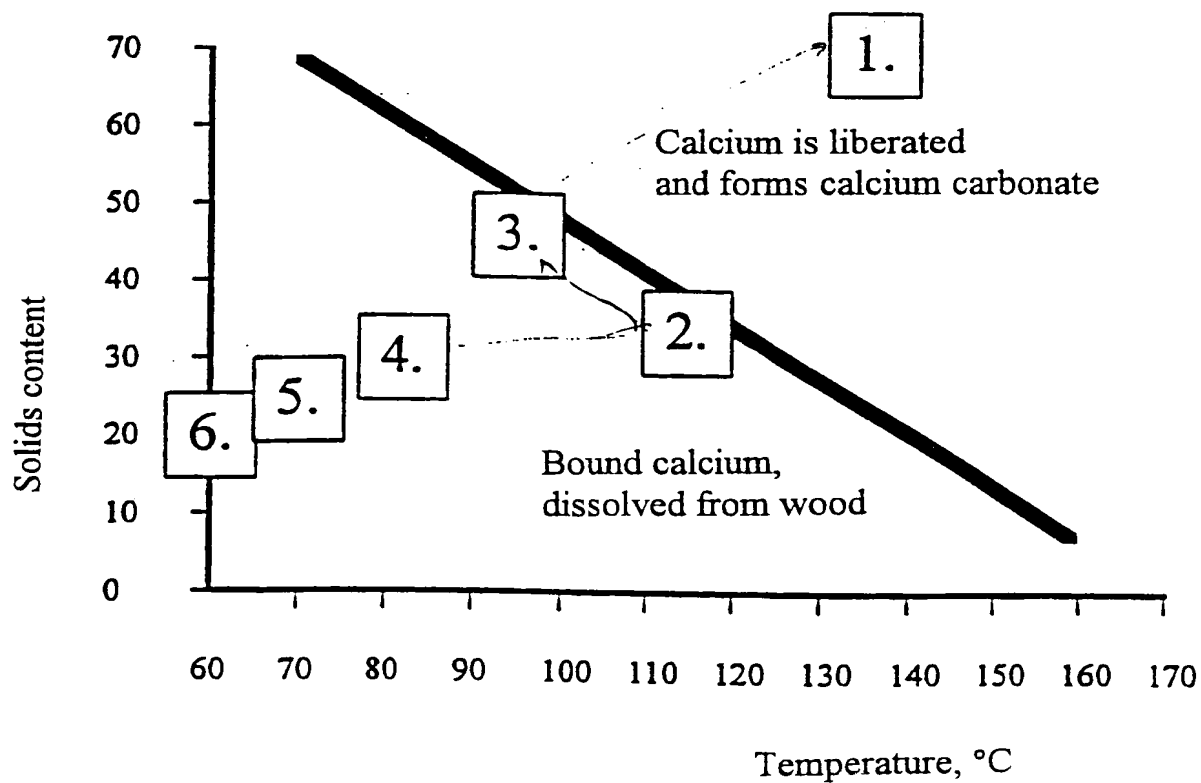
Altered black liquor flow sequence  
in a 6-stage evaporating plant



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Fig. 5

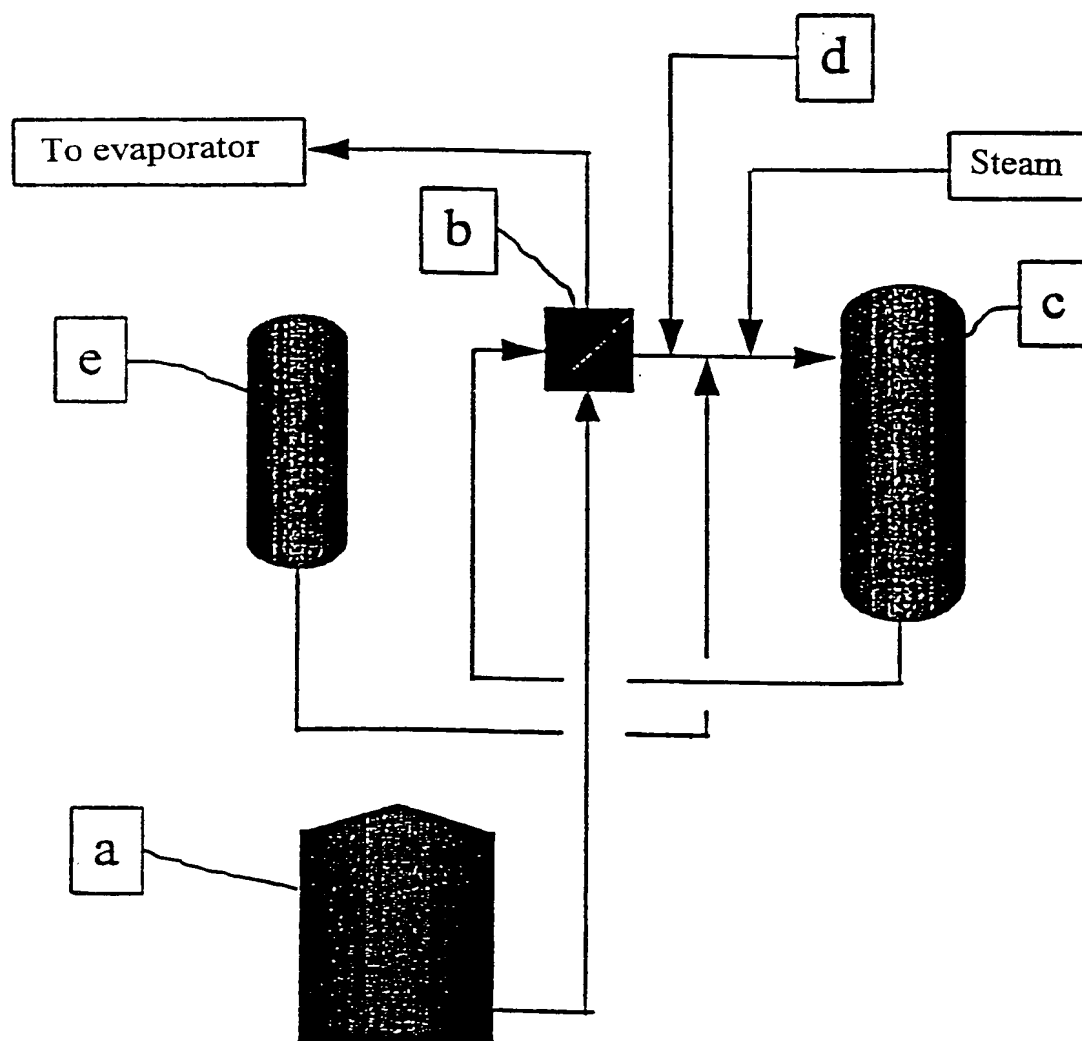
Altered solids/temperature change  
and critical limit in a 6-stage  
evaporation plant



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Fig. 6

Calcium deactivation at cooking plant

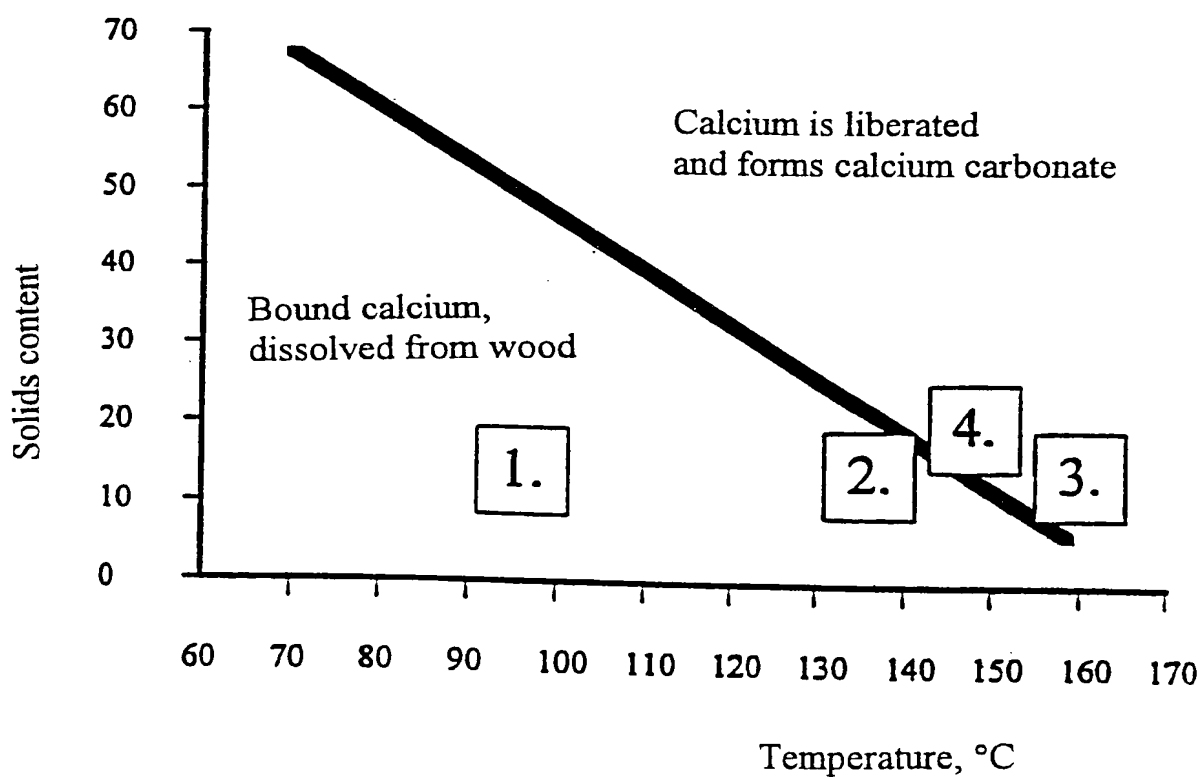




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Fig. 7

Calcium deactivation at cooking  
plant Solids/temperature change and  
critical limit



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00580

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 11/10, D21C 11/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI, FULLTEXT

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	--	2-3
Y	SE 153753 C (METALLGESELLSCHAFT AG), 13 March 1956 (13.03.56), page 4, column 1, line 65 - column 2, line 5, claim 1	2
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Y	US 5647955 A (JUKKA VAISTOMAA ET AL), 15 July 1997 (15.07.97), column 2, line 31 - line 34; column 3, line 21 - line 25, abstract	3
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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03/11/98

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